On the Quantum Theory<sup>\*</sup> of the Problem of the Two Bodies. (Preliminary Communication.) By J. R. OPPENHEIMER. (Communicated by Mr R. H. FOWLER.)

## [Read 26 July 1926.]

The problem of the two bodies has been treated on the new mechanics by Dirac\*, Pauli+, and Schrödingert, who have independently derived the Balmer terms. The present paper is an attempt at a more complete solution. In particular, formulae are derived for the line intensities of the hydrogen spectrum, for the photoelectric effect and its inverse, and for the continuous absorption spectrum in the ultraviolet and in the X-ray regions. Also the probabilities of transition, deflection and capture are computed for the collision of an electron and an ion. Numerical values are only obtained, however, for the simplest line intensities. It is hoped to treat the problem in greater detail.

I. Elliptic Orbits. For the line intensities the system may be treated as multiply periodic. We shall assume three degrees of freedom, and characterize transitions by six quantum numbers (nkm, n'k'm'). The fourth degree of freedom which would follow from the existence of an electronic magnetic moment, would not affect the intensities of the series lines as wholes. For the emission lines we may use the classical formula§ for the intensity in which frequencies and amplitudes have been replaced by their quantum theoretic analogues. Thus

$$I(nkm, n'k'm') = \sum_{\alpha=1}^{3} \frac{2^{4}\pi^{4}\epsilon^{2}}{3c^{3}} [\nu^{4}(n, n')] |x_{\alpha}(nkm, n'k'm')|_{i}^{2} \dots (1).$$

The frequencies are

$$\nu(nn') = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$
.....(2).

According to Schrödinger¶ the amplitudes are given by

$$x_a u (nkm) = \sum_{n' k' m'} \sum_{m' k' m'} x_a (nkm, n'k'm') u (n'k'm') \dots (3),$$

where the functions u(nkm) satisfy the following conditions:

1. They are bounded everywhere within the configuration space  $0 \leq r$ ;  $0 \leq \Im \leq \pi$ ;  $0 \leq \phi \leq 2\pi$ , and tend to zero sufficiently fast as  $r \rightarrow \infty$ .

- Dirac, Proc. Roy. Soc. A, 110, 561 (1926).
  Pauli, Zeit. f. Phys. 36, 336 (1926).
  Schrödinger, Ann. d. Phys. 79, 361 (1926).
  Kramers, Intensities of Spectral Lines, Copenhagen, 1919.
  Born u. Jordan Zeit. f. Phys. 34, 858 (1925).
  Schrödinger, Ann. d. Phys. 79, 734 (1926).

423

2. They are twice continuously differentiable.

3. They satisfy, if  $\mu$ ,  $\epsilon$  and E are mass, charge and energy of the electron

4. They are one-valued within the configuration space.

5. They are normal and orthogonal with respect to the configuration space

$$\iiint u(nkm)u(n'k'm')\rho dr d\vartheta d\phi = \delta_n^{n'} \delta_k^{k'} \delta_m^{m'}; \rho = \frac{\partial (x_1 x_2 x_3)}{\partial (r\phi \vartheta)}$$
$$= r^2 \sin \vartheta$$
....(5).

From this it follows that

$$x_{\alpha} (nkm, n'k'm') = \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} u (nkm) u (n'k'm') x_{\alpha} (r \Im \phi) \rho (r \Im \phi) d\phi d\Im dr \dots (6).$$

For E < 0, it is only possible to construct solutions which have the form

$$u(nkm) = u_{nkm}(r, \vartheta, \phi)$$

where  $\bar{k} = k - \frac{1}{2}$  and  $\alpha = (4\pi^2 \mu \epsilon^2 / nh^2) r$  satisfy (1)—(5) for certain values of the constants, namely

$$n = 1, 2, 3 \dots, , \\ \bar{k} = 0, 1, 2 \dots, (n-1) \\ m = 0, \pm 1, \pm 2 \dots, \pm \bar{k}$$
.....(8).

From (1), (6) and (7), we get, on performing the integrations, the selection rules

Averaging over m and m', we get the component intensities\*

$$I(nk, n'k') = \frac{2^{7} \pi^{8} \mu^{3} \epsilon^{14}}{3c^{3} h^{8} k} \left(\frac{1}{n'^{2}} - \frac{1}{n^{2}}\right)^{4} \frac{(k+k') A^{2}(nk, n'k')}{A^{2}(nk) A^{2}(n'k')} \dots (10).$$

\* The intensities of the hydrogen lines have been investigated by Pauli in a paper not yet published.

where .....

424

and

$$A^{2}(nk) = \sum_{\gamma_{1}=0}^{n-\bar{k}-1} \sum_{\gamma_{2}=0}^{n-\bar{k}-1} \frac{n^{3}(-1)^{\gamma_{1}+\gamma_{2}}(2k+\gamma_{1}+\gamma_{2}+1)! [(n+\bar{k})!]^{2}}{\gamma_{1}! \gamma_{2}! (2k+\gamma_{1})! (2k+\gamma_{2})! 2^{2k} (n-\bar{k}-1-\gamma_{1})! (n-\bar{k}-1-\gamma_{2})!}$$
....(11)

Averaging again over k and k' we get the series intensities. In ergs per atom per second these give\*, for the first and second Lyman lines, 0.00667 and 0.000644; for the first and second Balmer lines, 0.00789 and 0.00199. The only directly observable ratio is that of the second Lyman to first Balmer line. Thus

$$\frac{I(3, 2)}{I(3, 1)} = 12.2.$$

The absorption lines (n, n') from the initial state n, have total intensities<sup>+</sup>

times the corresponding emission intensities. This gives, for instance, the two observable ratios

$$\frac{I_{\rm abs}(1,2)}{I_{\rm abs}(1,3)} = 7.72; \quad \frac{I_{\rm abs}(2,3)}{I_{\rm abs}(2,4)} = 5.37.$$

The evidence in favour of such calculations of absolute intensities is not very extensive. Two such calculations were carried through on the Correspondence Principle. Thus Tolman<sup>‡</sup> found an approximate agreement for the outer lines of a vibration-rotation band in the infra red; and Kramers § found a rough value for the efficiency of an X-ray bulb.

II. Hyperbolic Orbits. It is possible to extend this method to the treatment of hyperbolic orbits. Classically the Fourier coefficients for the coordinates do not exist for these orbits. On

- Fowler, Phil. Mag. 50, 1079 (1925).
  Tolman and Badger, Phys. Rev. 27, 383 (1926).
  Kramers, Phil. Mag. 46, 836 (1923).

<sup>\*</sup> I am indebted to Mr J. T. Edsahl for checking these calculations.

the quantum theory the components corresponding to a transition between two hyperbolic orbits do not exist and we are forced to use the accelerations directly. For photoelectric transitions, however, the coordinate components may be found, and the intensities are derived from them in accordance with (1). Here, however,

$$v(n, E) = \frac{R}{n^2} + \frac{E}{h}$$
 .....(14),

where E is the positive energy of the hyperbolic orbit. The factors in the solution of (4) which depend on  $\Im$  and  $\phi$  are those given in (7). The values of k and m for which these satisfy the conditions (1)--(5), are

For all values of m and k it is possible to find an integral function f(E, k) of r satisfying (4), and which, for a set of values of E which become closer and closer as the configuration space is expanded, satisfy the conditions (1) to (4), and are orthogonal. The characteristic functions so obtained are

$$u(Ekm) = A_1 \frac{\cos m\phi}{\sin m\phi} P_{\overline{k}}^{(m)}(\cos \vartheta) f(Ek) \quad \dots \dots (16),$$

where

The coefficients are given, on the one hand, by the double circuit integrals<sup>†</sup>

$$2c_{\nu}(Ek) = \left[\int_{(\gamma, -\gamma)} (z+\gamma)^{\alpha_{2}-1} (z-\gamma)^{\alpha_{1}-1} dz\right]^{-1} \\ \times B(\alpha_{1}\alpha_{2}) \int_{(\gamma, -\gamma)} \frac{z^{\nu}}{\nu!} (z+\gamma)^{\alpha_{2}-1} (z-\gamma)^{\alpha_{1}-1} dz \quad \dots \dots (18), \dots$$

where

and on the other, by the recurrence formulae

$$\left\{ \begin{array}{l} (\nu^{2} + 2k\nu) c_{\nu} + 8\pi^{2}mh^{-2}(\epsilon^{2}c_{\nu-1} + Ec_{\nu-2}) = 0 \\ c_{0} = \frac{1}{2} B(\alpha_{1}, \alpha_{2}) = \frac{\Gamma(\alpha_{1})\Gamma(\alpha_{2})}{\Gamma(\alpha_{1} + \alpha_{2})} \end{array} \right\} \quad \dots (20).$$

† See, for an account of the mathematical methods, Schlesinger, Differentialgleichungen, Vieweg, 1922, and Whittaker and Watson, Modern Analysis, Cambridge, Chap. XIV. From these it follows that

where  $S_{\nu}$  is of degree  $\lfloor \frac{\nu}{2} \rfloor$  in *E*, and thus that the series defining *f* is absolutely convergent and real. Finally, *f* is given asymptotically for large values of  $(2\gamma r)$  by the expansion

$$f(Ek) \sim r^{\overline{k}} (-2\gamma r)^{-\alpha_1} e^{\gamma r} \Gamma(\alpha_1) \sum_{s=0}^{\infty} \frac{\Gamma(\alpha_1+s)}{\Gamma(s) \Gamma(\alpha_1-s)} (-2\gamma r)^{-s} -r^{\overline{k}} (-2\gamma r)^{-\alpha_1} e^{-\gamma r} \Gamma(\alpha_2) \sum_{s=0}^{\infty} \frac{\Gamma(\alpha_2+s)}{\Gamma(s) \Gamma(\alpha_2-s)} (+2\gamma r)^{-s} \dots (22),$$

which only fails when E is zero.

It is now possible to see in detail how this case differs from the periodic one. In the first place it follows from (22) that we can no longer choose the constant  $s_1$  to make

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} u^2 \rho d\phi \, d\Im \, d\nu = 1.$$

The functions u are thus still orthogonal, but cannot be made normal. In the second place, even if we eliminate all values of Efor which condition 1 is not satisfied, we are left with a continuous manifold of characteristic functions. The equations (3) thus become meaningless, and must be replaced by

Here the  $u_n$  are to be normalized, and the  $u_E$  chosen to make  $x_a(Ekm, nk'm') = x_a'(nk'm', Ekm)....(24).$ 

Finally we may determine f(E) by the following argument.

Classically we should have, for the acceleration of the electron in an orbit of energy E,

$$\ddot{x}_a(E) = \int_{-\infty}^{\infty} \ddot{x}_a(E, \nu) \exp(2\pi i \nu t) d\nu,$$

and, for the energy radiated from that orbit

const. 
$$\sum_{a=1}^{3} \int_{-\infty}^{\infty} \ddot{x}_{a}^{2} (E\nu) \exp(2\pi i\nu t) d\nu.$$

Quantum theoretically we have, for the components of acceleration corresponding to a photoelectric transition

$$u(n)\ddot{x}_{a} = \int_{0}^{\infty} 4\pi^{2}\nu^{2}(nE) x_{a}(nE) u(E) \exp[2\pi i(E/h)t] df(E)$$
  
=  $\int_{0}^{\infty} \left[ 4\pi^{2}\nu^{2}(nE) x_{a}(nE) \frac{\partial f(E)}{\partial E} \cdot h \right] u(E) \exp[2\pi i(E/h)t] d(E/h)$   
.....(25)

[we suppress the indices k and m throughout this argument].

By analogy the radiated energy should be

const. 
$$\sum_{a} \int_{0}^{\infty} \left[ hx_{a}(nE) \nu^{2}(nE) \frac{\partial f(E)}{\partial E} \right]^{2} u(E) \exp \left[ 2\pi i(E/h)t \right] d(E/h),$$

so that the energy radiated per unit time from the transition  $n \rightarrow (E, E + dE)$  is, for given k + m, k' + m',

const. 
$$\sum_{a} \left[ hx_a(nE) \nu^2(nE) \frac{\partial f}{\partial E} \right]^2 d(E/h) \dots (26).$$

On the other hand the total radiation from inverse photoelectric transitions from an orbit of energy E is

const. 
$$\sum_{a} \sum_{n} x_{a}^{2} (En) \nu^{4} (En).$$

Of this

const. 
$$\sum_{a} x_a^2(En) \nu^4(En) \dots (27)$$

is to be ascribed to transitions  $E \rightarrow n$ .

Now for the fully excited atom, where all temperature factors are ironed out, the number of atoms in any range of phases will be proportional to the corresponding volume of phase space. Thus if the number of atoms in an elliptic orbit with quantum numbers nkm is one, the number with a given m and k and positive energy between E and  $E + \Delta E$  is

Here J is an action variable for the system and w the canonically conjugate angle variable. The rate at which this number is increasing is, since J is a constant,

$$w \frac{\partial J}{\partial E} \Delta(E/h)$$
 .....(29).

It is easy to shew that

Thus the number of electrons entering the range of hyperbolic orbits per unit time is

 $\Delta (E/h)$ .

This gives, for the condition for detailed equilibrium

 $x_a^2(nE) \nu^4(nE) \Delta(E/h) = [f'h x_a(nE) \nu^2(nE)]^2 \Delta(E/h) \dots (31),$ whence

We may verify<sup>\*</sup> this result in part by computing how many electrons enter the range of hyperbolic orbits

E,  $E + \Delta E$ ; k,  $k + \Delta k$ , m,  $m + \Delta m$ 

from a free electron gas with Maxwellian distribution-in-velocity. We get

const. 
$$\Delta E \cdot \Delta m \cdot (1 - m^2/k^2)^{-\frac{1}{2}} k \Delta k (k^2 + n^2)^{-\frac{1}{2}} \dots \dots (33).$$

In the limit of large (E and k) this becomes

const.  $\Delta E \Delta m \Delta k (1 - m^2/k^2)$ .

This agrees with the quantum theoretic calculation except for the factor  $(1 - m^2/k^2)^{-\frac{1}{2}}$ . The experiment of Stern and Gerlach suggests that, in this paradox, the quantum theoretic answer is right.

In any case (32) gives

(a) 
$$u(n) x_a = \sum_{n'=1}^{\infty} x_a(nn') u(n') + \int_0^{\infty} x_a(nE) u(E) d(E+h)$$
  
(b)  $u(E) x_a = \sum_{n'=1}^{\infty} x_a(En') u(n') + \int_0^{\infty} x_a(EE') u(E') d(E'+h) \int_0^{\infty} .....(34)$ 

to determine u(E) and thus the  $x_a(uE)$ . Let us call the factor in u which remains after division by the normalized functions of  $\mathfrak{F}$  and  $\phi$ ,  $\overline{u}$ ; and let us write

From (3) and (6) we get

$$r(En) = \int_0^\infty r^2 \cdot r \cdot u(E) \cdot u(n) dr = r_0(En) \chi(Ek) \dots (36).$$

Also,

where, for (36) and (37)

$$\int_0^\infty r^2 u^2(n)\,dr=1.$$

\* I am much indebted to Dr P. A. M. Dirac for suggesting this procedure.

Then we get, from (34), (36), (24) and (37), the integral equation for  $\chi$ 

$$u(n) r - \sum_{n'=1}^{\infty} r(nn') u(n') = \int_{0}^{\infty} \chi^{2}(Ek) f(Ek; r) r_{0}(En) d(E/h)$$
.....(38),

which is of the form

$$\int_0^\infty \chi^2(En) F_1(r; E, n, k, k') d(E/h) = F_2(r; n, k') \dots (39).$$

The existence of a solution (38) independent of r is made plausible by the orthogonality of the u(E); the mathematical problem will be treated in detail shortly.

With this notation the continuous absorption spectrum is given by

$$I(nk, nk') dE = \frac{2^{7} \pi^{5} \epsilon^{2} \mu (k'+k)}{3c^{3} h^{2} k} \left(\frac{E}{h} + \frac{R}{n^{2}}\right) \frac{\chi^{2} (Ek) \alpha^{2}}{\beta} dE \quad \dots (40),$$

where

$$\begin{aligned} \alpha &= \sum_{\nu=0}^{\infty} \sum_{\gamma=0}^{n-\bar{k}-1} \left( -\frac{4\pi^2 \mu \epsilon^3}{nh^2} \right)^{-(\nu+k+k'+j+3)} \\ & c_{\nu} \left( Ek' \right) \frac{(-2)^j}{\gamma !} \binom{n+\bar{k}}{n-\bar{k}-1-j} (\nu+k+k'+j+2) \, ! \\ \beta &= \left( \frac{4\pi^2 \mu \epsilon^2}{\bar{h}^2} \right)^{-2\bar{k}-3} A^2 (n,k) \\ \mathrm{d} & |k-k'| = 1. \end{aligned}$$

and

Moreover, if  $\rho(\nu)$  is the energy density of radiation, the distribution of photoelectrons in velocity per atom per unit of time is

Similarly the emission spectrum from hyperbolic to elliptic orbits is, in energy per electron

$$I(Ek, nk') = \frac{2^4 \pi^4 \epsilon^2}{3c^3} \left(\frac{E}{h} + \frac{R}{n^2}\right)^4 \frac{k+k'}{k} \frac{(\alpha \chi)^2}{\beta} \dots \dots (42),$$
$$|k-k'| = 1.$$

It follows from (22) that the integrals for the components of the coordinates corresponding to transitions between two hyperbolic orbits diverge. If we compute the components of the acceleration directly from the equations of motion we get

$$\ddot{x}_a = \varpi_a \epsilon^2 \mu^{-1} r^{-2}$$
  
$$\varpi_1 = \cos \phi \sin \vartheta; \quad \varpi_2 = \sin \phi \sin \vartheta; \quad \varpi_3 = \cos \vartheta$$
.....(43),

from which

$$= \overset{a}{} \mu \ddot{x}_a \left( Ekm E' k' m' \right) d \left( E'/h \right)$$
  
=  $d \left( E'/h \right) \iiint \sin \Im \varpi_a u \left( Ekm \right) u \left( E'k'm' \right) d\phi d\Im d\nu \dots (44).$ 

Now

$$\int_{0}^{\infty} f(Ek) f(E'k') d\nu \simeq \sum_{\nu=0}^{\infty} g_{\nu} R_{1}^{\nu+k+k'+1}; \ g_{\nu} = \sum_{\tau=0}^{\nu} \frac{c_{\tau}(Ek)_{\nu} c_{\nu-\tau}(E'k')}{\nu+k+k'}$$
.....(45),

where we must choose  $R_1$  to make

 $2\gamma(E)R_1 >> 1; 2\gamma(E')R_1 >> 1.$ 

For small values of E, of the order of a volt, the series converges rapidly.

This gives, for the intensity of the continuous emission spectrum

$$I(Ek, E'k') d(E'/h) = \frac{2^4 \pi^4 \epsilon^2}{3c^3} \frac{k+k'}{k} \chi^{-1}(Ek) \chi^{-1}(E'k') \sum_{\nu=0}^{\infty} g_{\nu} R_1^{\nu+k+k'+1} d(E'/h)$$
(46).

III. Kinematics. From (42) and (46) we can get the probability that an electron, entering an hyperbolic orbit, shall be bound to the ion in an elliptic orbit, or shall emerge in another hyperbolic orbit. These probabilities are equal to the corresponding intensity of radiation divided by the energy radiated for a single transition. The total probability of capture for an electron of energy E and total angular momentum k, averaged over the possible values of m, is thus

Classically an angular momentum k would correspond to an hyperbola with asymptote a distance  $\Delta$  from the origin

Thus an electron of energy E must "fall within a circle of area  $\frac{\pi\epsilon^4}{4E^3}$  about the ion." Its probability of capture is

The quantity called, classically, the effective cross-section, is, for such electrons

Now, classically the electron approximates more and more closely to a free electron as r is indefinitely increased. This is not, however, true on the new theory. For it is easy to shew, by setting  $\epsilon = 0$  in (4), that the characteristics for the free electron are

which, for large r, approach

On the other hand (22) gives, for large r, characteristics which differ from (52) by having  $(\gamma r + in' - h\gamma r)$  in place of  $(\gamma r)$ .

Now it will in general be possible to expand the self adjoint characteristics  $u\sqrt{\rho}$  for large r in terms of the characteristics for electrons moving with velocity  $\left(\frac{h\gamma}{2\pi\mu}\right)$  in three normal directions in space. If it should be possible to expand\* it in terms of the

In space. If it should be possible to expand it in terms of the characteristics of only such electrons as have the same energy, this would solve the problem of the deflection spectrum. For the initial beam we should have such a sum of characteristics as would give an electron moving, say, along the x axis with the initial velocity. During the encounter the statistical distribution of the characteristics will be changed, in accordance with (46). By analysis of the resulting characteristics in terms of the characteristics of free electrons with the corresponding final energy moving along the three normal directions, we can find the relative probability of any deflection and change in energy by the encounter  $\uparrow$ . This problem will be considered in detail.

I should like to thank Mr R. H. Fowler, F.R.S. and Dr P. A. M. Dirac, for many valuable suggestions.

- \* This is impossible if one neglects transitions.
- † In this connection see a paper by Born, Zeit. f. Phys. 37, 863 (1926).